Unexpected effects of mesoporosity on the catalytic performance of ZSM-5 for the fast pyrolysis of cellulose to aromatic hydrocarbons

Hoff, Thomas C.; Gardner, David W.; Thilakaratne, Rajeeva; Proano-Aviles, Juan; Hansen, Thomas Willum; Brown, Robert C.; Tessonnier , Jean Philippe

Publication date:
2017

Document Version
Peer reviewed version

Unexpected effects of mesoporosity on the catalytic performance of ZSM-5 for the fast pyrolysis of cellulose to aromatic hydrocarbons

Thomas C. Hoff,[1] David W. Gardner,[1] Rajeeva Thilakaratne,[2] Juan Proano-Aviles,[2] Thomas W. Hansen,[3] Robert C. Brown,[2] Jean-Philippe Tessonnier[1]

[1]Chemical and Biological Engineering, Iowa State University, Ames, IA, United States
[2]Bioeconomy Institute, Iowa State University, Ames, IA, United States
[3]Center for Electron Nanoscopy, Technical University of Denmark, Lyngby, Denmark

Catalytic fast pyrolysis (CFP) represents a sustainable method to convert raw biomass into useful chemicals and fuels in a single step. ZSM-5 has been identified as the best catalyst for this reaction, producing hydrocarbons with a high selectivity to benzene, toluene, xylene, and naphthalene. Yet, the corresponding yields remain low (~ 30 C%) and a signification fraction of carbon is lost in the form of coke. It has been hypothesized that coke formation is primarily due to transport limitations and may be addressed by introducing mesopores in the zeolite crystals. We tested this hypothesis by synthesizing mesoporous ZSM-5 through top-down (desilication of commercial zeolite) and bottom-up (laboratory synthesized samples) methods. Our results revealed a significantly more complex interplay of various parameters, including crystallinity, elemental composition, porosity, and acidity. The introduction of mesopores was typically accompanied by an alteration of the zeolite's structure and the formation of amorphous species that hinder the diffusion of bulky oxygenates under reaction conditions. Combining ten different characterization techniques revealed that crystallinity and aluminum site accessibility are critical to achieve high aromatic yields. As a result, large microporous ZSM-5 crystals afford higher aromatic hydrocarbon yields than mesoporous ZSM-5.

1. T. C. Hoff, D. W. Gardner, R. Thilakaratne, K. Wang, T. W. Hansen, R. C. Brown, J.-P. Tessonnier, Tailoring ZSM-5 Zeolites for the Fast Pyrolysis of Biomass to Aromatic Hydrocarbons, *ChemSusChem*, **2016**, *9*, 1473-1482. http://dx.doi.org/10.1002/cssc.201600186

2. T. C. Hoff, R. Thilakaratne, D. W. Gardner, R. C. Brown, J.-P. Tessonnier, Thermal Stability of Aluminum-Rich ZSM-5 Zeolites and Consequences on Aromatization Reactions, *J. Phys. Chem. C*, **2016**, *120*, 20103-20113. http://dx.doi.org/10.1021/acs.jpcc.6b04671

3. T. C. Hoff, D. W. Gardner, R. Thilakaratne, J. Proano-Aviles, R. C. Brown, J.-P. Tessonnier, Elucidating the Effect of Desilication on Aluminum-Rich ZSM-5 Zeolite and Its Consequences on Biomass Catalytic Fast Pyrolysis, *Appl. Catal. A*, **2017**, *529*, 68-78. http://dx.doi.org/10.1016/j.apcata.2016.10.009